Mechanochemical polymerization of diphenylamine (DPA) was performed in solvent-free condition by employing two different oxidizing agents namely ammonium peroxydisulfate (APS) and ferric chloride (FC) in the presence of different protonating agents namely HCl, H$_2$SO$_4$ and H$_3$PO$_4$. The effect of the above-said oxidizing agents and protonating agents on the physicochemical properties of as prepared polydiphenylamine (PDPA) are explained and the results are presented on a comparative basis in this chapter.

### 3.1. INTRODUCTION

Polyaniline (PANI) has gained attention as a technologically important material in rechargeable batteries, sensors, electrochromic display devices and corrosion protection [1–4], due to its good electrochemistry [5], electrochromism [6], good environmental stability in air [7] and ease of preparation in both aqueous acid and organic media. In order to improve the processibility [8–10], electrochromism and other properties of PANI [11–13], polymers derived from various benzene ring substituted and $N$-substituted aniline derivatives were investigated extensively. Polymers of $N$-substituted aniline derivatives, such as $N$-methyl, $N$-ethyl, $N$-phenyl, $N$-naphthyl and $N$-benzyl were obtained through electrochemical method [11–16]. On reviewing these reports, few generalization trends could be observed relating to the electropolymerization of $N$-substituted anilines. It is found that the oxidation potential for these $N$-substituted aniline class of monomers is lower than aniline. Also, the anilinium cation type radicals produced from their derivatives have been reported to be relatively more stable than those formed from aniline, as a result of the presence of
electron donating group at the N-position. These in-built characteristics are expected to induce new properties for the poly(N-substituted aniline) in comparison with PANI. Literature search reveals that majority of these studies were devoted on the polymerization of N-methyl aniline. N-aryl aniline derivatives were electrochemically polymerized in acetonitrile solution [11,14]. The mechanism for electropolymerization of DPA in acetonitrile was also studied in detail [15]. The polymerization of DPA has been reported to be different from other N-substituted anilines. While polymerization has been reported to proceed through the formation of the N-C coupling in the case of other N-substituted anilines, polymerization of DPA is known to proceed through the 4,4’-phenyl-phenyl coupling mechanism [15]. An extraordinarily high rate is expected for the polymerization of DPA due to the benzidine type of reactions during polymerization. PDPA is found to show many properties that are not comparable with other N-substituted aniline derivatives, which include electrochemistry, conductivity and electrochromism [14,15].

Although PDPA can be prepared by electropolymerisation methods, the most common route is chemical oxidative polymerization from monomers in solutions. However, DPA is widely regarded as a monomer unsuitable for oxidative polymerisation using milder reagents/solvents in conventional solution-phase synthetic method owing to its poor solubility. Hence, in the process of finding a simple, rapid, sustainable and effective alternative method, we have developed a newer solvent-free mechanochemical route to prepare high quality PDPA and some of its salts. The synthetic strategy adopted and physicochemical properties of all the resultant polymeric materials are elaborated in the following sections.
3.2. MECHANOCHEMICAL POLYMERIZATION OF DPA

3.2.1. Synthesis of doped/undoped PDPA

1.7 g of solid DPA was taken in a glass mortar and was hand-ground for 5 minutes using a pestle. To this finely grounded DPA, 2.2 g of solid APS or 2.7 g of solid FC was added. After the addition of the oxidant, the solid phase mixture was further hand-ground immediately for 20 minutes until the colour of the product turned dark green. The formed polymeric product was washed thoroughly with water, methanol and diethyl ether. After repetitive washings, the polymer was dried in vacuum oven at 40ºC for 12 h. The purified dry PDPA powder prepared in the presence of APS and FC individually was used for further characterization.

The preparation of doped PDPA involves the addition of 0.5 ml of doping agent (37 wt.% HCl / 96 wt.% H2SO4 / 87 wt.% H3PO4) to 1.7 g of solid DPA in a glass mortar. This monomer-doping agent reactant mixture was thoroughly hand-ground for 30 minutes in order to achieve homogeneity. The rest of the polymerization procedure was followed as given above. The purified PDPA salts obtained employing APS and FC as oxidants were used for performing further studies. Herein, undoped PDPA is termed as PDPA, PDPA doped with HCl as PDPA-HCl, PDPA doped with H2SO4 as PDPA- H2SO4 and PDPA doped with H3PO4 as PDPA- H3PO4.

3.2.2. Elemental analysis, yield and processibility

The percentage composition of C, H and N is consistent with the repeat unit composition of C12H9N in all of the prepared PDPA samples. The presence of Cl, S and P in PDPA-HCl, PDPA-H2SO4 and PDPA-H3PO4 respectively suggests the doping of respective anions has taken place in the polymeric backbone due to the usage of different acids during their preparative process (table 3.1). Interestingly, it
could be noticed that undoped PDPA prepared using APS has 0.35% sulphur which might be due to the self-doping during the course of mechanochemical polymerisation with APS. However, S to N ratio of 0.04 indicates negligible doping of PDPA. In a similar fashion, undoped PDPA prepared using FC has 0.33% chlorine due to the self-doping of chorine present in FC. From the highest S to N ratio observed from table 3.1, it could be noted that doping level of PDPA-H₂SO₄ is found to be more than the other doped counterparts in both cases of APS and FC. This may be attributed to the fact that polyprotic nature and strong oxidisability of H₂SO₄ favours the doping process more than the other protic acids employed for mechanochemical polymerization reaction. Moreover DPA is found to react more readily with 96 wt.% H₂SO₄ rather than 37 wt.% HCl and 87 wt.% H₃PO₄ due to the strong protonating capability of H₂SO₄. Unlike aniline, DPA does not react well with HCl and is found to react less readily with H₃PO₄. This argument goes in agreement with the elemental composition analysis data. The order of doping level as followed from table 3.1 in both APS and FC systems is PDPA-H₂SO₄ > PDPA-HCl > PDPA-H₃PO₄. It can be seen from table 3.2 that the yield obtained for all PDPA salts are comparable to each other. As expected, PDPA prepared in the absence of protonating agent in both APS and FC has resulted in a comparatively lesser amount of polymer than the other polymers. This may be due to the creation of lesser radical centers for the polymerization reaction to proceed. All of the as prepared PDPA salts are found to be highly dispersible in common solvents like ethanol, acetone and double distilled water. This dispersion tends to turn unstable only after considerable period of time. These observations indicate the processable nature of all the doped PDPA powders. From the above scientific evidences, it could be concluded that the facile solid-state
method does assists in the preparation of pure and processible PDPA salts in appreciable quantity in both of the tested oxidants.

3.2.3. FTIR spectra

Fig. 3.1A (a-d) shows the FTIR spectra of PDPA salts synthesized by solid-state polymerization method using APS as oxidant. The characteristic peak at ~3387-3391 cm$^{-1}$ is caused by the N-H stretching mode of the secondary amine. The strong peak at ~1595-1598 cm$^{-1}$ can be assigned to the different bending mode of the aromatic secondary amine [17-19]. The peak at ~1502-1508 cm$^{-1}$ is characteristic of the C-C multiple bond stretching mode of benzene ring [20]. The C-N stretching mode of the aromatic secondary amine causes the peak at ~1316-1319 cm$^{-1}$. The peak at ~1172-1176 cm$^{-1}$ can be assigned for the C-H bending vibration of diphenoquinone [21]. The sharp peaks at ~746-750 and ~690-695 cm$^{-1}$ is assigned for the terminal phenyl groups and C-H out-of-plane phase bending vibration of mono-substituted benzene rings at the ends of the polymer chains respectively. The vibrational bands located in the range of 610, 567 and 490 cm$^{-1}$ is associated with (PO$_4$)$_3^-$ and (SO$_4$)$_2^-$ groups. The results indicate that the backbone structures of PDPA-HCl, PDPA-H$_2$SO$_4$, and PDPA-H$_3$PO$_4$ obtained in this solid state synthesis method are identical to each other and also to those of PDPA salts synthesized previously in conventional chemical and electrochemical methods [21,22].

Fig. 3.1B (a-d) shows the FTIR spectra of PDPA salts synthesized by solid-state polymerization method using FC as oxidant. All the bands observed in fig.1A are found to appear in these spectra suggesting the polymer backbone is very similar to that of PDPA prepared using APS oxidant (table 3.3). From the characteristic peaks noticed in the FTIR spectrum, it can be concluded that the mechanochemical route has successfully yielded high quality pristine PDPA and its doped forms.
3.2.4. UV–Vis absorption spectra

Fig. 3.2A (a-d) represents the UV–Vis absorption spectra of PDPA and its salts prepared using APS dispersed in DMF solution. The spectral profile show two characteristic absorption peaks at ~335-337 nm, ~535-550 nm. The well-defined peak at ~335-337 nm can be ascribed to $\pi-\pi^*$ electronic transition of the benzenoid rings in the polymer backbone, while the broad peak at ~535-550 nm (inset of fig.3.2A) can be attributed to polaron–$\pi^*$ transition, characteristic of dipheno quinine dimine form (scheme 3.1) of PDPA or bipolaronic state of PDPA [23,24].

Fig. 3.2B (a-d) shows the UV–Vis absorption spectra of PDPA and its salts prepared using FC dispersed in DMF solution. Here too, one sharp peak at ~335-341 nm and the other broad peak at ~490-507 nm (inset of fig. 3.2B) could be noticed for all the polymers. The intensity of polaron–$\pi^*$ peak roughly indicates the amount of polaronic chain present in the polymer backbone. It could be observed that irrespective of oxidant used for polymerization, PDPA prepared using $\text{H}_2\text{SO}_4$ as doping agent shows more intense polaron–$\pi^*$ band. This may be due to the more oxidative ability and polyprotic nature of 96 wt.% $\text{H}_2\text{SO}_4$ in comparison with the other doping acids. From these results, it can be said with conformity that $\text{H}_2\text{SO}_4$ serves as better doping agent among the tested protic acids for preparing PDPA with better electronic properties.

3.2.5. XRD pattern

Crystallinity and orientation of conducting polymers have been of much interest, because more highly ordered systems could display a metallic-like conductive state. The powder diffractograms of the different samples of PDPA prepared by APS and FC are shown in fig.3.3A (a-d) and 3.3B (a-d). The two major
diffraction peaks in the range of $2\theta = 18.15^\circ$-18.41$^\circ$ and 22.67$^\circ$-22.84$^\circ$ found in the X-ray diffraction patterns of doped PDPA prepared using APS (fig.3.3A (a-d)) could be attributed to the periodicity parallel to the polymer chain and periodicity perpendicular to polymer chain respectively. The latter peak is stronger in the case of PDPA-H$_2$SO$_4$ [fig. 3.3A (c)] indicative of the formation of PDPA in a highly doped conducting state compared to the other polymers. There were no or very less intense peaks in the diffraction pattern of PDPA and PDPA-H$_3$PO$_4$. This shows the formation of polymeric backbone with no or very less doping in these cases.

The XRD profile of the mechanochemically synthesized PDPA and its salts using FC possess ordered systems appreciably better than those reported in the literature adopting any synthetic methodology [11,14,15]. The relatively sharp and stronger diffraction peaks at $2\theta = \sim 11-13^\circ$, 18°, 20° and 25° can be found in the XRD spectrum of PDPA and its salts. It can be followed from fig. 3.3B (b-d) that there is a medium intense reflex around 11-13° in all of the doped PDPA. These reflexes could be due to the presence of closely packed benzene rings. The reflexes at around 20° is rendered by the periodicity parallel to the polymer chain and that around 25° is caused by the periodicity perpendicular to the polymer chain. The former peak is also reported to represent the distance between the ring planes of benzene rings in adjacent chains or the close contact inter-chain distance [25]. On close examination of the peak at around 20° and 25°, it could be noticed that the same peaks for PDPA-H$_2$SO$_4$ is stronger than that of the remaining polymers indicating that it is in a highly doped state.
3.2.6. Morphology

The simple and greener synthetic route adopted to synthesize PDPA yielded polymeric products with distinctly different morphologies. Fig. 3.4A (a-d) displays the FESEM image of PDPA and its salts prepared using APS. Since the mechanochemical polymerization is a surface confined process, the nature of reacting species plays a vital role in influencing the morphology of the formed polymeric particles. As seen in the FESEM images of PDPA and its salts, formation of aggregates of polymeric particles could be noticed. Fig. 3.4A (a) shows PDPA-HCl particles with an average size of 90 nm. These polymeric particles were highly aggregated with lamellar structure. Fig. 3.4A (b) displays PDPA-H2SO4 particles with an average size of 100 nm. The micromorphology of PDPA-H3PO4 [fig.3.4A (c)] shows bigger non-uniform microstructured particles. Similarly the image of undoped PDPA [fig.3.4A (d)] also highlights the presence of particulates with an average size of 100 nm. The morphological difference is due to the difference in interaction between the reactants employed in the polymerization with APS. The influence of mechanical forces on the parent reagents and reaction products greatly influence the morphological feature of PDPA and its salts.

FESEM image of PDPA-HCl [fig. 3.4B (a)] is found to possess nanorods along with few disc shaped polymeric particles. Random accumulation of nanorods could be seen in the same micrograph. The majority of PDPA-HCl particles were found as fused nanorods with sizes ranging from 35 to 50 nm. Inset picture in fig. 3.4B (a), indicates the presence of nanorods with random dimensions. Few rods have much higher thickness, shorter length and hence appear as nanodiscs. It is important to note that the nanorods/nanodiscs are rigid and are well separated. Fig. 3.4B (b) presents the FESEM image of PDPA-H2SO4 which has leafy structures with
sizes ranging from 25-30 nm. This particular morphology is quite distinct from that of PDPA-HCl. Even though the methodology adopted to produce the polymer is same, depending on the nature of the reacting species and the surface that is on offer for the mechanochemical reaction to precede the morphology differs. H$_2$SO$_4$ used as dopant in this case, is presumed to offer reaction environment suitable for the polymeric particles to align in a more regular fashion inducing the formation of uniformly distributed leafy structures closely associated with each other [inset of fig. 3.4B (b)]. There are some areas where aggregation of PDPA-H$_2$SO$_4$ leaves could be noticed. This might have resulted from the exposure of initially formed polymeric fractions to mechanochemical process for a longer time. The surface morphological feature of PDPA-H$_3$PO$_4$ [fig. 3.4B (c) and its inset] consists of fine network of highly interconnected PDPA-H$_3$PO$_4$ nanofibers. The nanofibers are found to have an average size of 20 nm. Meanwhile, fig. 3.4B (d) showing the PDPA particles witnesses the formation of irregular aggregates along with the presence of nanoparticles with indefinite shape. The absence of doping agent in the reaction might have hindered the formation of uniform polymeric particles with definite shape and size. From these FESEM pictures, it is very easy to comprehend the fact that the role of doping agent plays a crucial role in the formation of different nanostructures while adopting this greener solid phase reaction route for synthesizing PDPA nanoparticles.

3.2.7. Electrochemical activity

The electrochemical activity of the PDPA and its salts was investigated with cyclic voltammetry. As expected, cyclic voltammogram (CV) without any characteristic peak is obtained for plain GCE in 0.5 mol/L H$_2$SO$_4$ [fig. 3.5A (a)]. Fig. 3.5A (b-e) shows the CVs of the polymer films (fabricated from PDPA prepared
using APS) on GCE in 0.5 mol/L H$_2$SO$_4$. The anodic and cathodic potentials are listed in table 3.5. Two redox couples are observed in the CVs of PDPA salts, while only one redox couple is in the CV of PDPA. The first redox peak in the positive sweep (at 0.46 V) is well-known as the feature indicating the formation of N,N’-diphenyl benzidine type radical cation (polaronic form of PDPA) and the second redox peak at 0.79–0.99V is the formation of N,N’-diphenyl benzidine dication (bipolaronic form of PDPA) through the oxidation of PDPA salts [26]. The redox peaks are relatively sharp in CVs of PDPA-HCl and PDPA-H$_2$SO$_4$ than PDPA-H$_3$PO$_4$. However, broad peaks and more positive shift in the redox potential are observed in the CV of PDPA which may be due to the absence of dopants in the polymer backbone.

The redox behaviour of PDPA and its doped forms prepared by using FC is displayed in fig. 3.5B (b-e). The CVs of the PDPA films features a pair of redox peaks. The CV of PDPA [fig. 3.5B(b)] gave rise to two oxidation peaks, one at ~0.47 V with lesser current and the other at ~0.91 V with higher current along with a reduction peak at ~0.38 V. The former peak is assigned to the generation of N,N’-diphenyl benzidine type radical cation (polaronic form of PDPA) and the latter to the N,N’-diphenyl benzidine dication (bipolaronic form of PDPA). For PDPA-HCl [fig. 3.5B(c)], two oxidation peaks at ~0.45 V and ~0.86 V, a reduction peak at ~0.48 V is observed. In the case of PDPA-H$_2$SO$_4$ [fig. 3.5B (d)], one redox couple (at 0.44 and 0.48V) and a sharp peak at 0.86V could be noticed. The oxidation peak for PDPA-H$_3$PO$_4$ is appearing at ~1.13 V [fig. 3.5B (e)] shows a shift in the oxidation peak potential value. This may be the effect of larger size of the dopant anion bound to the polymeric structure [27]. Moreover PDPA-H$_3$PO$_4$ is found to be in a more oxidized state due to the higher pH value of H$_3$PO$_4$. The CVs recorded for PDPA and
its salts prepared through the mechanochemical route suggest the formation of redox-active PDPA salts.

### 3.2.8. Conductivity

The conductivity of PDPA and its salts prepared by APS and FC is listed in table 3.6. As expected PDPA prepared by employing APS or FC is found to be less conductive rather than its salts. PDPA-H\textsubscript{2}SO\textsubscript{4} is found to possess higher conductivity than other salts irrespective of the oxidant employed for solid-state polymerization. From the results of FTIR spectra, UV–Vis spectra and cyclic voltammogram studies, the conductivity differences of PDPA salts is dependent on the characteristics of doping agents used viz., HCl, H\textsubscript{2}SO\textsubscript{4} and H\textsubscript{3}PO\textsubscript{4}. Since 96 wt.% H\textsubscript{2}SO\textsubscript{4} is more oxidative, polyprotic and strong acid and since it forms salt more readily with DPA compared to other acids used, PDPA-H\textsubscript{2}SO\textsubscript{4} is found to show better conductivity.

### 3.2.9. Thermal stability

The thermal curves obtained from thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of PDPA, PDPA-HCl, PDPA-H\textsubscript{2}SO\textsubscript{4} and PDPA-H\textsubscript{3}PO\textsubscript{4} are presented in fig. 3.6A (a-d) respectively. The first step loss (5-8%) in all polymers occurred at 60\textdegree C due to the loss of trapped water molecules present in the polymer matrix. The second step loss (12-13%) observed at 220\textdegree C-300\textdegree C is due to the loss of dopants and low molecular weight fragments of the polymer. The absence of such thermal event for PDPA [fig. 3.6A (a)] confirms the conjecture that HCl/H\textsubscript{2}SO\textsubscript{4}/H\textsubscript{3}PO\textsubscript{4} ion, which are present as dopant ions, are removed in this temperature range. Degradation of PDPA main chain starts from 300\textdegree C as observed for both doped and undoped samples. Doped PDPA shows similar weight losses at temperature beyond 400\textdegree C. DTA curves of doped polymer shows two exothermic peaks at 445-500\textdegree C and 700-750\textdegree C. The former exotherm is due to the thermal
expulsion of dopants present in the polymer chain and latter is due to the thermal
degradation of polymer. These results are in good agreement with the reported values [26].

3.3. CONCLUSIONS

PDPA doped with inorganic acids (e.g., HCl, H$_2$SO$_4$ and H$_3$PO$_4$) were
synthesized by solid-state polymerization by using APS or FC. Elemental analysis
proved the presence of corresponding dopant anions [Cl$^-$, (SO$_4$)$_2^-$, (PO$_4$)$_3^-$] in the
polymeric backbone of PDPA prepared using APS or FC. The yield obtained from
this reaction route is found to be appreciable. All of the prepared PDPA salts were
processible using common solvents like water and acetone. Spectroscopic studies
showed the presence of quinoid and benzenoid units in all doped forms of PDPA and
emeraldine phase is formed predominantly in all PDPA salts. These results were
further supported by conductivity measurements and cyclic voltammetry. More
crystalline PDPA salt was obtained by doping with H$_2$SO$_4$ in comparison with other
protic acids used in both the cases of APS and FC. FESEM pictures depicted
formation of more uniform nanostructures for PDPA salts prepared using FC.
Anhydrous metal salts have extended one- or two- dimensional structures. The
mechanical grinding is found to increase the number of new surface for coordination
with iron ions and also improves the interfacial diffusion of the products that has
resulted in the formation of nanostrutures. All the as-prepared PDPA salts are found
to be thermally stable up to 300°C. Among these inorganic acids, H$_2$SO$_4$ was found to
be more suitable as a protonating/doping acid for preparing PDPA salt with high
conductivity through this mechanochemical route irrespective of the oxidants (APS or
FC) employed for the polymerization procedure. These differences in the properties of
the PDPAs mainly depended on the characteristics of inorganic acids (e.g., HCl,
H$_2$SO$_4$ and H$_3$PO$_4$): small amount of water in the acids; strong and weak oxidizability of the acids. All these lead to PDPA salts with different physicochemical properties.
REFERENCES


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   119.
Table 3.1. Elemental composition of PDPA and its salts

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<tr>
<th>Polymer</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>% O</th>
<th>% Cl</th>
<th>% S</th>
<th>% P</th>
<th>Cl/N or S/N or P/N ratio</th>
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<td>PDPA</td>
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<td>--</td>
<td>--</td>
<td>0.16</td>
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<tr>
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<td>8.05</td>
<td>8.61</td>
<td>--</td>
<td>2.24</td>
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<td>--</td>
<td>--</td>
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Table 3.2. Yield of PDPA and its salts

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<th>Yield in %</th>
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<tr>
<td>PDPA</td>
<td>64</td>
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<tr>
<td>PDPA-HCl</td>
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Table 3.3. Assignment of bands found in FTIR spectra of PDPA and its salts

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<tr>
<th>Polymer</th>
<th>(N-H)s</th>
<th>(N-H)b</th>
<th>(C-C)s</th>
<th>(C-N)s</th>
<th>(C-H)b</th>
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<td>1597</td>
<td>1502</td>
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<td>1596</td>
<td>1503</td>
<td>1316</td>
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<td>PDPA prepared using FC</td>
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### Table 3.4. Assignment of UV-Vis absorption peaks of PDPA and its salts

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<th>Polaron–$\pi^*$ band (nm)</th>
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<tr>
<td>PDPA</td>
<td>337</td>
<td>540</td>
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<td>PDPA-HCl</td>
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<td>535</td>
</tr>
<tr>
<td>PDPA- H$_2$SO$_4$</td>
<td>335</td>
<td>581</td>
</tr>
<tr>
<td>PDPA-H$_3$PO$_4$</td>
<td>335</td>
<td>551</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\pi-\pi^*$ band (nm)</th>
<th>Polaron–$\pi^*$ band (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDPA</td>
<td>334</td>
<td>507</td>
</tr>
<tr>
<td>PDPA-HCl</td>
<td>335</td>
<td>505</td>
</tr>
<tr>
<td>PDPA- H$_2$SO$_4$</td>
<td>341</td>
<td>496</td>
</tr>
<tr>
<td>PDPA-H$_3$PO$_4$</td>
<td>335</td>
<td>490</td>
</tr>
</tbody>
</table>

### Table 3.5. The redox potentials of PDPA and its salts

<table>
<thead>
<tr>
<th>Polymer</th>
<th>First redox peak $E_{pa}/V$</th>
<th>$E_{pc}/V$</th>
<th>Second redox peak $E_{pa}/V$</th>
<th>$E_{pc}/V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDPA</td>
<td>--</td>
<td>--</td>
<td>0.99</td>
<td>0.53</td>
</tr>
<tr>
<td>PDPA-HCl</td>
<td>0.46</td>
<td>0.36</td>
<td>0.81</td>
<td>0.52</td>
</tr>
<tr>
<td>PDPA- H$_2$SO$_4$</td>
<td>0.45</td>
<td>0.36</td>
<td>0.78</td>
<td>0.48</td>
</tr>
<tr>
<td>PDPA-H$_3$PO$_4$</td>
<td>0.46</td>
<td>0.37</td>
<td>0.79</td>
<td>0.51</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polymer</th>
<th>First redox peak $E_{pa}/V$</th>
<th>$E_{pc}/V$</th>
<th>Second redox peak $E_{pa}/V$</th>
<th>$E_{pc}/V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDPA</td>
<td>0.46</td>
<td>0.38</td>
<td>0.91</td>
<td>--</td>
</tr>
<tr>
<td>PDPA-HCl</td>
<td>0.77</td>
<td>0.40</td>
<td>0.96</td>
<td>0.50</td>
</tr>
<tr>
<td>PDPA- H$_2$SO$_4$</td>
<td>0.44</td>
<td>0.48</td>
<td>0.86</td>
<td>--</td>
</tr>
<tr>
<td>PDPA-H$_3$PO$_4$</td>
<td>--</td>
<td>--</td>
<td>1.13</td>
<td>0.97</td>
</tr>
</tbody>
</table>

### Table 3.6. Conductivity values of PDPA and its salts

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDPA</td>
<td>0.02</td>
</tr>
<tr>
<td>PDPA-HCl</td>
<td>0.55</td>
</tr>
<tr>
<td>PDPA- H$_2$SO$_4$</td>
<td>0.90</td>
</tr>
<tr>
<td>PDPA-H$_3$PO$_4$</td>
<td>0.22</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDPA</td>
<td>0.06</td>
</tr>
<tr>
<td>PDPA-HCl</td>
<td>0.95</td>
</tr>
<tr>
<td>PDPA- H$_2$SO$_4$</td>
<td>1.12</td>
</tr>
<tr>
<td>PDPA-H$_3$PO$_4$</td>
<td>0.68</td>
</tr>
</tbody>
</table>
Scheme 3.1. Redox states of PDPA: (a) fully reduced form, (b) polaronic form and (c) bipolaronic form
Fig. 3.1A. FTIR spectra of PDPA and its salts prepared using APS: (a) PDPA (b) PDPA-HCl (c) PDPA-H$_2$SO$_4$ and (d) PDPA-H$_3$PO$_4$.
Fig. 3.1B. FTIR spectra of PDPA and its salts prepared using FC: (a) PDPA (b) PDPA-HCl (c) PDPA-H$_2$SO$_4$ and (d) PDPA-H$_3$PO$_4$
Fig. 3.2A. UV-Vis spectra of PDPA and its salts prepared using APS: (a) PDPA (b) PDPA-HCl (c) PDPA-H_2SO_4 and (d) PDPA-H_3PO_4
Fig. 3.2B. UV-Vis spectra of PDPA and its salts prepared using FC: (a) PDPA (b) PDPA-HCl (c) PDPA-H$_2$SO$_4$ and (d) PDPA-H$_3$PO$_4$
Fig. 3.3A. XRD pattern of PDPA and its salts prepared using APS: (a) PDPA (b) PDPA-HCl (c) PDPA-H$_2$SO$_4$ and (d) PDPA-H$_3$PO$_4$
Fig. 3.3B. XRD pattern of PDPA and its salts prepared using FC: (a) PDPA (b) PDPA-HCl (c) PDPA-H$_2$SO$_4$ and (d) PDPA-H$_3$PO$_4$
Fig. 3.4A. FESEM image of PDPA and its salts prepared using APS:
(a) PDPA-HCl (b) PDPA-H$_2$SO$_4$ (c) PDPA-H$_3$PO$_4$ and (d) PDPA
Fig. 3.4B. FESEM image of PDPA and its salts prepared using FC: (a) PDPA-HCl (b) PDPA-H$_2$SO$_4$ (c) PDPA-H$_3$PO$_4$ and (d) PDPA
Fig. 3.5A. Cyclic voltammograms of PDPA and its salts prepared using APS: (a) Plain GCE (b) PDPA/GCE (c) PDPA-HCl/GCE (d) PDPA-H$_2$SO$_4$/GCE and (d) PDPA-H$_3$PO$_4$/GCE
Fig. 3.5B. Cyclic voltammograms of PDPA and its salts prepared using FC: (a) Plain GCE (b) PDPA/GCE (c) PDPA-HCl/GCE (d) PDPA-H$_2$SO$_4$/GCE and (d) PDPA-H$_3$PO$_4$/GCE
Fig. 3.6A. TG/DTA curves of PDPA and its salts prepared using APS: (a) PDPA (b) PDPA-HCl (c) PDPA-H$_3$SO$_4$ and (d) PDPA-H$_3$PO$_4$
Fig. 3.6B. TG/DTA curves of PDPA and its salts prepared using FC: (a) PDPA (b) PDPA-HCl (c) PDPA-H₂SO₄ and (d) PDPA-H₃PO₄